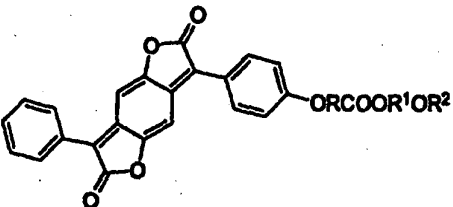
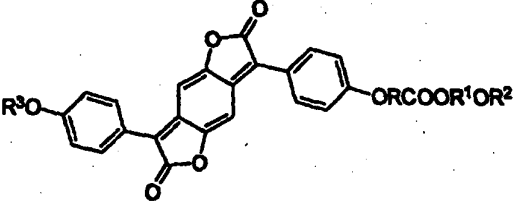
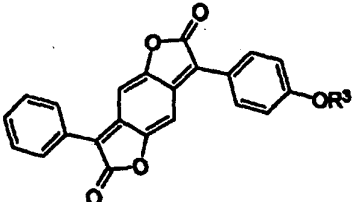


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(54) Title: DYE MIXTURES (57) Abstract A disperse dye mixture which comprises, on a weight basis, from 5 % to 70 % of the dye of Formula (1), from 5 % to 70 % of the dye of Formula (2), and from 0 % to 40 % of the dye of Formula (3), wherein each of R and R ¹ represents an alkylene group and each of R ² and R ³ represents an alkyl group.			
<div style="text-align: right;">  (1) </div> <div style="text-align: right;">  (2) </div> <div style="text-align: right;">  (3) </div>			

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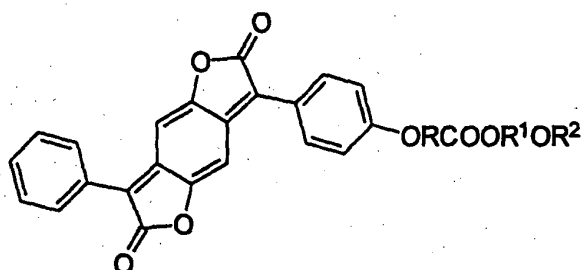
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DYE MIXTURES

The present invention relates to a mixture of dyes, particularly a mixture of disperse polycyclic dyes, to a process for the coloration of synthetic textile materials and to textile materials when coloured with the mixture of dyes.

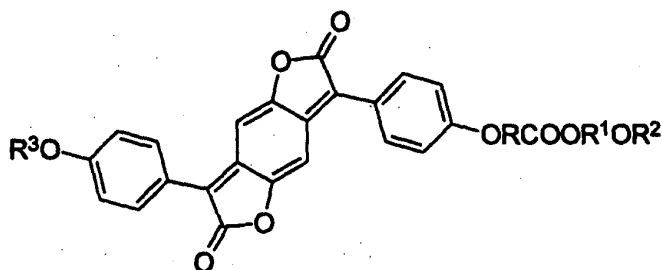
Polycyclic dyes are known (EP 0033583 and EP 0146269) and may be applied to synthetic textile materials by various dyeing techniques such as exhaust or continuous dyeing or printing. Generally, textile materials, when dyed or printed with such dyes, exhibit very high levels of wet-fastness. However, it is difficult to achieve heavy shades on textile materials with these dyes particularly when exhaust dyeing is carried out at 130°C, the most common temperature for batch dyeing polyester. Under these conditions, yields and levelling are usually poor and exhaustion is relatively low with much of the dye remaining in the dyebath. This poor performance can be overcome to some extent by increasing the dyeing temperature but not sufficiently to allow trouble free dyeing.

According to the present invention, there is provided a disperse dye mixture which comprises, on a weight basis, from 5% to 70% of the dye of Formula (1):



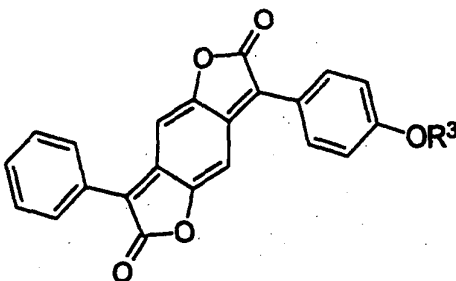
Formula (1)

from 5% to 70% of the dye of Formula (2)



Formula (2)

and from 0% to 40% of the dye of Formula (3):



Formula (3)

wherein each of R and R¹ represents an alkylene group and each of R² and R³ represents an alkyl group.

The alkylene groups represented by R and R¹ are preferably C₁₋₈-alkylene groups, more preferably C₁₋₆-alkylene groups and especially C₁₋₄-alkylene groups. It is especially preferred that R is methylene and R¹ is methylene or ethylene.

The alkyl groups represented by R² and R³ are preferably C₁₋₆-alkyl groups more preferably C₁₋₄-alkyl groups and especially C₁₋₄-alkyl groups. It is especially preferred that R² is methyl or ethyl and R³ is propyl.

The present dye mixture has improved dyeing properties and allows heavy depths of shade to be obtained at 130°C with improved levelling properties and improved exhaustion over commercially available dyes. Furthermore, the dye mixture provides a commercially popular shade.

The dye mixture preferably comprises from 5% to 70%, more preferably from 10% to 30%, by weight of the dye of Formula (1), from 5% to 70%, more preferably from 40% to 60%, by weight of the dye of Formula (2) and from 5% to 40%, more preferably from 10% to 35%, by weight of the dye of Formula (3).

An especially preferred dye mixture comprises from 16% to 21% by weight of the dye of Formula (1), from 50% to 55% by weight of the dye of Formula (2) and from 26% to 31% by weight of the dye of Formula (3).

An especially preferred mixture of dyes comprises a dye of Formula (1) in which R is -CH₂-, R¹ is -C₂H₄- and R² is -C₂H₅, a dye of Formula (2) in which R is -CH₂-, R¹ is -C₂H₄-, R² is -C₂H₅ and R³ is n-propyl and a dye of Formula (3) in which R³ is n-propyl.

The mixture of dyes according to the invention may be a simple physical mixture or may be mixed crystals formed, for example, by co-crystallisation or co-synthesis. Crystalline modifications of compounds of Formulae (1), (2) and (3) exist and it is intended that the present definition includes such crystalline modifications which may be formed by established treatments such as heat treatment, solvent treatment, recrystallisation or seeding.

According to a further feature of the present invention, there is provided a process for colouring a synthetic textile material or fibre blend thereof which comprises applying to the synthetic textile material a disperse dye mixture as hereinbefore defined.

5 The synthetic textile material may be selected from secondary cellulose acetate, cellulose triacetate, polyamide, polyacrylonitrile and aromatic polyester. The synthetic textile material is preferably polyamide such as polyhexamethylene adipamide or aromatic polyester, especially polyethylene terephthalate. Fibre blends may comprise mixtures of different synthetic textile materials or mixtures of synthetic and natural textile materials. Preferred fibre blends include those of polyester cellulose such as polyester-cotton. The textile materials or blends thereof may be in the form of filaments, loose
10 fibres, yarn or woven or knitted fabrics.

The mixture of dyes according to the invention, optionally in conjunction with other disperse dyes, may be applied to the synthetic textile materials or fibre blends thereof by processes which are conventionally employed in applying disperse dyes to
15 such materials and fibre blends.

Suitable process conditions include the following:

- i) exhaust dyeing at a pH of from 4 to 6.5, at a temperature of from 125°C to 140°C for from 10 to 120 minutes and under a pressure of from 1 to 2 bar, a sequestrant optionally being added;
- 20 ii) continuous dyeing at a pH of from 4 to 6.5, at a temperature of from 190°C to 225°C for from 15 seconds to 5 minutes, a migration inhibitor optionally being added;
- iii) printing direct at a pH of from 4 to 6.5, at a temperature of from 160°C to 185°C for from 4 to 15 minutes for high temperature steaming, or at a
25 temperature of from 190°C to 225°C for from 15 seconds to 5 minutes for bake fixation with dry heat or at a temperature of from 120°C to 140°C and 1 to 2 bar for 10 to 45 minutes for pressure steaming, wetting agents and thickeners (such as alginates) of from 5 to 100% by weight of the dye optionally being added;
- 30 iv) discharge printing (by padding the dye on to the textile material, drying and overprinting) at a pH of from 4 to 6.5, migration inhibitors and thickeners optionally being added;
- v) carrier dyeing at a pH of from 4 to 6.5, at a temperature of from 95°C to 100°C using a carrier such as methylnaphthalene, diphenylamine or 2-phenylphenol, sequestrants optionally being added.
35

In all the above processes, the mixture of dyes according to the invention is applied as a dispersion comprising from 0.001% to 4% by weight of the dye mixture in aqueous medium.

Compositions comprising dispersions of the disperse dye mixture of the invention form a further feature of the present invention. The compositions typically comprise from 1% to 30% by weight of a mixture of the dyes in an aqueous medium. The compositions are preferably buffered at pH 2 to 7, more preferably at pH 4 to 6.

5 The dye dispersions may further comprise ingredients conventionally used in coloration applications such as dispersing agents, for example lignosulphonates, naphthalene sulphonic acid/formaldehyde condensates or phenol/cresol/sulphanilic acid/formaldehyde condensates, surfactants, wetting agents such as alkyl aryl ethoxylates which may be sulphated, sulphonated or phosphated, inorganic salts, de-foamers such as mineral oil or nonanol, organic liquids and buffers. Dispersing agents
10 may be present at from 10% to 200% on the weight of the dye mixture. Wetting agents may be used at from 0% to 20% on the weight of the dye mixture. The dispersions may be prepared by bead milling the dye mixture with glass beads or sand in an aqueous medium or by combining dispersions of milled dyes.

15 Dispersions may be dried, after the addition of any extra dispersing agents, to give a solid physical form with from 5 to 60% by weight of total colour.

 In addition to the above-mentioned application processes, the dye mixtures of the invention may be applied to synthetic textile materials and fibre blends by ink-jet printing, the substrates optionally having been pre-treated to aid printing. For ink-
20 jet applications, the application medium may comprise water and a water-soluble organic solvent, preferably in a weight ratio of 1:99 to 99:1, more preferably 1:95 to 50:50 and especially in the range 10:90 to 40:60. The water-soluble organic solvent preferably comprises a C₁-C₄-alkanol, especially methanol or ethanol, a ketone, especially acetone, methyl ethyl ketone, 2-pyrrolidone or N-methylpyrrolidone, a glycol, especially ethylene
25 glycol, propylene glycol, trimethylene glycol, butane-2,3-diol, thiodiglycol or diethylene glycol, a glycol ether, especially ethylene glycol monomethyl ether, propylene glycol monomethyl ether or diethylene glycol monomethyl ether, urea, a sulphone, especially bis-(2-hydroxyethyl) sulphone or mixtures thereof.

 The dye mixture may also be applied to textile materials using
30 supercritical fluid solvents, for example supercritical carbon dioxide, in which case the dye formulating agents may optionally be omitted.

 The dyes of Formulae (1), (2) and (3) may be prepared by the processes described in EP 0033583 and EP 0146269.

 The invention is further illustrated but not limited by the following
35 Examples in which all percentages are by weight:

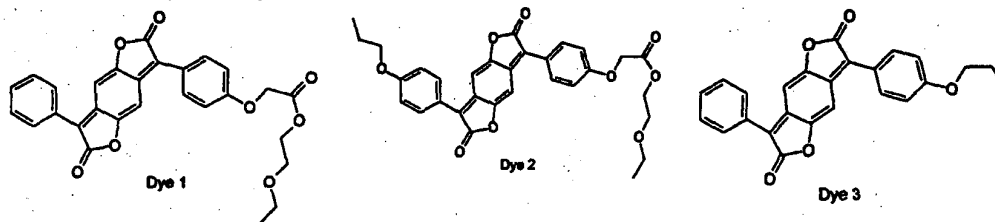
Example 1

 A mixture comprising 18.8% of Dye 1, 52.6% of Dye 2 and 28.6% of Dye 3 was prepared and used to dye polyester textile material by an exhaust dyeing technique

at 130°C. The degree of exhaustion was measured by comparing the amount of dye initially added to the dyebath with that remaining after dyeing, when twice the amount of dye needed to achieve a 1/1 Standard Depth of shade was initially employed. Comparison was by solution measurement using an absorption Spectrophotometer, capable of measuring the concentration of dye in solution in the visible region of the Electromagnetic Spectrum. The degree of exhaustion was >90%.

The levelling property was assessed by measuring the reflectance of a dyed piece of polyester fibre at 1/1 Standard Depth of Shade. This value was taken as 100%. This was compared with the reflectance from an initially undyed piece of polyester, which was held for 1 hour at 130°C in a blank dyebath in the presence of an identical dyed piece, and the dye transferred to the undyed piece was expressed as a percentage of the original dyed piece.

Dyes 1, 2 and 3 have the structures shown below, Dye 1 being a dye of Formula (1), Dye 2 a dye of Formula (2) and Dye 3 a dye of Formula (3):



Comparative Example A

A preparation using only one dye (Dye 3) was used to dye polyester textile material under identical conditions to those used in Example 1 and to an equivalent depth of shade. The degree of exhaustion was less and the levelness of the dyeing was inferior compared with the dye mixture of the invention used in Example 1.

Comparative Example B

A preparation using only one dye (Dye 2) was used to dye polyester textile material under identical conditions to those used in Example 1 and to an equivalent depth of shade. The degree of exhaustion was less and the levelness of the dyeing was inferior compared with the dye mixture of the invention used in Example 1.

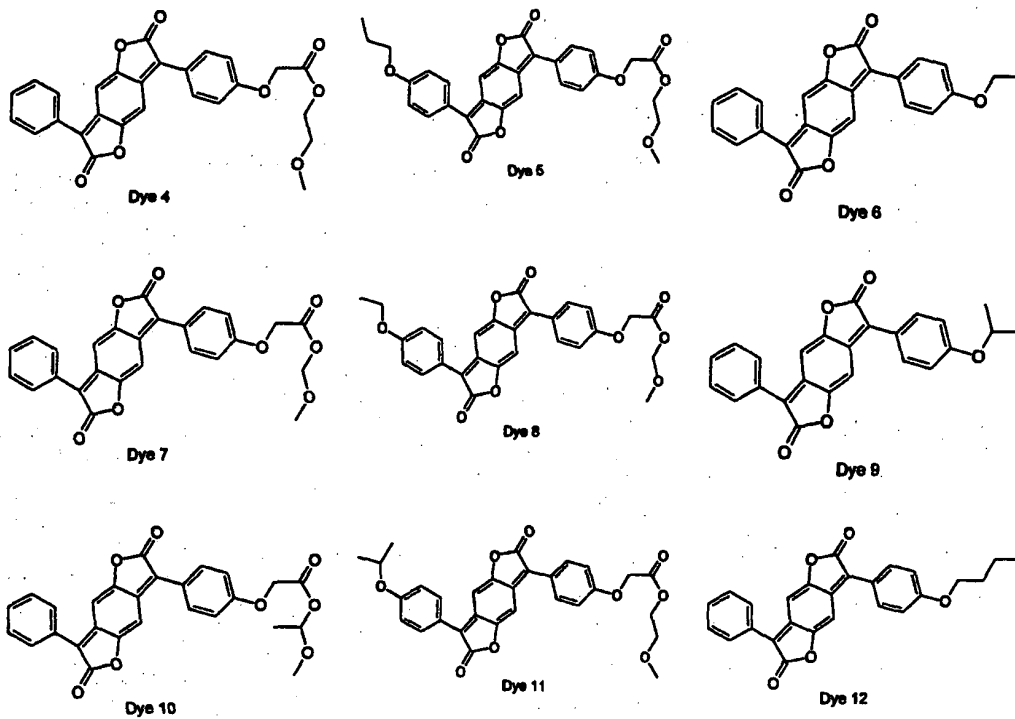
Examples 2-17

Further dye mixtures based on Dyes 1, 2 and 3, described in Example 1, were applied to polyester textile material under the conditions described in Example 1. There again showed superior exhaustion and level dyeing properties compared with the single dyes used in Comparative Examples A and B. The mixtures had the following compositions:

Example	% of Dye 1	% of Dye 2	% of Dye 3
2	33	67	0
3	10	60	30
4	12	55	33
5	14	55	31
6	16	55	29
7	17	52	31
8	19	54	27
9	20	55	25
10	20	50	30
11	25	50	25
12	25	60	15
13	27	48	25
14	30	55	15
15	30	40	30
16	30	65	5
17	30	60	10

Examples 18-42

5 Further mixtures of dyes were prepared. The dyes had the following structures, Dyes 4, 7 and 10 being dyes of Formula (1), Dyes 5, 8 and 11 being dyes of Formula (2) and Dyes 6, 9 and 12 being dyes of Formula (3):



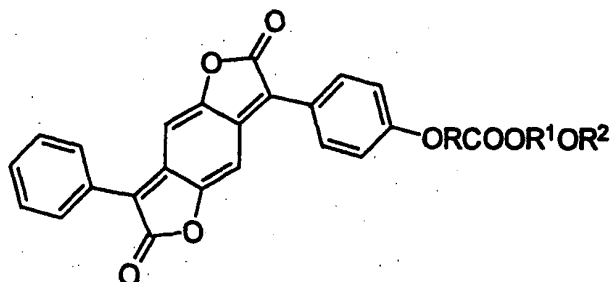
5 Mixtures of the above dyes were applied to polyester in the same manner as in Example 1, as follows:

Example	% of Dye 4	% of Dye 5	% of Dye 6	% of Dye 7	% of Dye 8	% of Dye 9	% of Dye 10	% of Dye 11	% of Dye 12
18	12	55	33						
19	16	55	29						
20	14				55	31			
21		54		19		27			
22		50		25		25			
23			25	20	55				
24		52		17					31
25							30	55	15
26	12				55				33
27		55		16					29
28			29		55		16		
29			33	12				55	
30				16	55	29			
31							12	55	33
32							16	55	29
33	27	48	25						
34				27	48	25			
35							27	48	25
36	19				54				27
37	19	54				27			
38				24	59				17
39	18.8				52.6				28.6
40				18.8	52.6				28.6
41		52.6				28.6	18.8		
42			28.6	18.8				52.6	

These mixtures again showed level dyeing and exhaustion properties superior to the individual components.

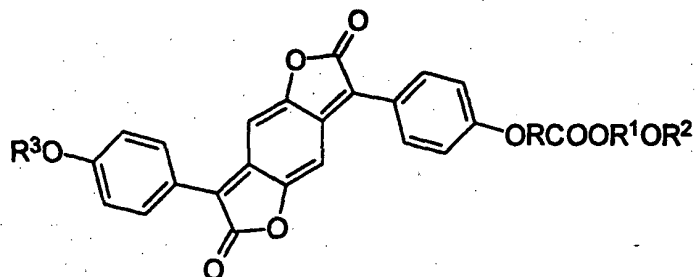
CLAIMS

1. A disperse dye mixture which comprises, on a weight basis, from 5% to 70% of the dye of Formula (1):



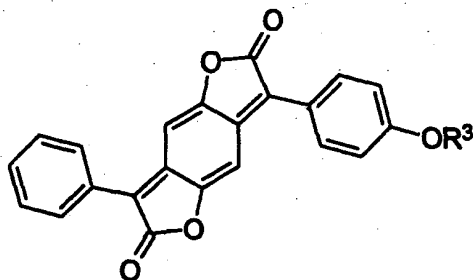
Formula (1)

from 5% to 70% of the dye of Formula (2):



Formula (2)

and from 0% to 40% of the dye of Formula (3):



Formula (3)

- wherein each of R and R¹ represents an alkylene group and each of R² and R³ represents an alkyl group.

2. A dye mixture according to Claim 1 which comprises from 5% to 70% by weight of the dye of Formula (1), from 5% to 70% by weight of the dye of Formula (2) and from 5% to 40% by weight of the dye of Formula (3).

3. A dye mixture according to Claim 2 which comprises from 10% to 30% by weight of the dye of Formula (1), from 40% to 60% by weight of the dye of Formula (2) and from 10% to 35% by weight of the dye of Formula (3).
- 5 4. A dye mixture according to Claim 3 which comprises from 16% to 21% by weight of the dye of Formula (1), from 50% to 55% by weight of the dye of Formula (2) and from 26% to 31% by weight of the dye of Formula (3).
- 10 5. A dye mixture according to any one of Claims 1 to 4 wherein in the dye of Formula (1) R is $-\text{CH}_2-$, R^1 is $-\text{C}_2\text{H}_4-$ and R^2 is $-\text{C}_2\text{H}_5$, in the dye of Formula (2) R is $-\text{CH}_2-$, R^1 is $-\text{C}_2\text{H}_4$, R^2 is $-\text{C}_2\text{H}_5$ and R^3 is n-propyl, and in the dye of Formula (3) R^3 is n-propyl.
- 15 6. A process for colouring a synthetic textile material or fibre blend thereof which comprises applying to the synthetic textile material a dye mixture as defined in claim 1.
- 20 7. A process according to Claim 6 which comprises applying to the synthetic textile material a dye mixture as defined in claim 2.
8. A composition comprising from 1% to 30% by weight of a dye mixture as defined in Claim 1 dispersed in an aqueous medium.
- 25 9. A composition according to Claim 8 containing from 1% to 30% by weight of a dye mixture as defined in Claim 2.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/01532

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09B67/22 C09B57/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09B D06P

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X X Y	EP,A,0 492 893 (ICI PLC) 1 July 1992 see page 4, line 49 - line 55 see the whole document ---	1 1 1-9
Y	EP,A,0 598 303 (SUMITOMO CHEMICAL CO) 25 May 1994 see abstract; examples ---	1-9
Y	EP,A,0 146 269 (ICI PLC) 26 June 1985 cited in the application see abstract; examples ---	1-9
A	EP,A,0 574 148 (ZENECA LTD) 15 December 1993 see abstract -----	1-9

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☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 96/01532

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0492893	01-07-92	CA-A- 2058087	22-06-92
		JP-A- 4309565	02-11-92
		US-A- 5220040	15-06-93
EP-A-0598303	25-05-94	JP-A- 6200178	19-07-94
		US-A- 5413613	09-05-95
EP-A-0146269	26-06-85	GB-A,B 2151611	24-07-85
		HK-A- 51089	30-06-89
		JP-A- 6049071	22-02-94
		JP-B- 6057712	03-08-94
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		JP-C- 1552145	23-03-90
		JP-A- 60152567	10-08-85
		US-A- 4650882	17-03-87
EP-A-0574148	15-12-93	JP-A- 6065516	08-03-94